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(54) Title: PREPARATION OF LOW MOLECULAR WEIGHT CELLULOSE ESTERS

## (57) Abstract

A process is disclosed for the preparation of low molecular weight, high hydroxyl cellulose esters ideally suited for use in coating applications. The new synthetic procedure involves treating a cellulose polymer with trifluoroacetic acid, a mineral acid, an acyl or aryl anhydride in an appropriate carboxylic solvent followed by, optionally, in situ hydrolysis. Typical reaction times for conversion to a triester are 5 to 30 minutes while typical hydrolysis times for far hydrolyzed mixed esters range from 4 to 7 hours. Molecular weight loss occurs during formation of the cellulose triester permitting concentrated reaction mixtures and easier isolation of the product ester.

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## PREPARATION OF LOW MOLECULAR WEIGHT CELLULOSE ESTERS

Field of Invention

This invention relates to the preparation of  
5 cellulose esters. In one aspect, it relates to the  
preparation of cellulose triesters. In another aspect,  
it relates to the preparation of cellulose esters with a  
degree of substitution (DS) less than three. In yet  
another aspect, it relates to the preparation of low  
10 molecular weight cellulose esters.

Background of the Invention

Cellulose esters are of great commercial  
importance. Cellulose acetates, for example, are used  
15 in cigarette filters and as photographic film base.  
Other cellulose esters, e.g., cellulose propionates,  
cellulose butyrates, cellulose acetate propionates, or  
cellulose acetate butyrates, have found widespread use  
in cosmetics, plastics, and pharmaceuticals.  
20 Furthermore, cellulose esters, in particular, cellulose  
mixed esters having low molecular weight and high  
hydroxyl content, have high commercial utility as  
coatings resins (P.M. Cook, U.S. Patent 4,839,230  
(1989)). These low molecular weight and high hydroxyl  
25 containing cellulose esters provide for high solids to  
liquid ratios in coating formulations, provide reactive  
sites for crosslinking reactions, and suitable  
functionality for derivatization of the cellulose  
polymer. Therefore, an improved process for the  
30 production of cellulose esters suitable for coating  
applications would be of considerable commercial  
importance.

It is well known in the art that cellulose  
triesters, for example cellulose triacetate (DS = 3; the  
35 degree of substitution is defined as the number of acyl

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groups per anhydroglucose ring), can be prepared by treating preactivated cellulose with a mixture of sulfuric acid, acetic acid, and acetic anhydride (H.L.B. Gray and C.J. Staud, U.S. Patent 1,683,347 (1928)).

5 Cellulose triacetate is not suitable for all uses and, consequently, is often hydrolyzed to a cellulose acetate with a degree of substitution of 0.6-2.8 (C.J. Malm, U.S. Patent 1,984,147 (1934); C.R. Fordyce, U.S. Patent 2,129,052 (1938)). Such a process requires dilute  
10 reaction mixtures, long reaction times, and requires isolation of the high boiling by-product acetic acid from the dilute reaction mixture.

In U.S. Patent 1,880,808 (1932), H.T. Clarke and C.J. Malm disclose the use of chloro, bromo, or alkoxy  
15 containing acetyl anhydrides as an impelling reagent (i.e., an anhydride which promotes esterification without contributing any groups to the ester produced) in the esterification of cellulose with fatty acids. In a typical procedure, cellulose was treated with an  
20 excess (1.9-9.1 equivalents per hydroxyl) of the impelling reagent, the appropriate fatty acid, and a catalyst. After the required reaction time, the product was isolated by precipitation into a nonsolvent. Such a  
25 process typically requires a large excess of the impelling reagent and produces only the cellulose triester. Furthermore, isolation of the high boiling impelling acid from a dilute solution which also contains the esterifying fatty acid is required. Similar work disclosed by H.T. Clarke and C.J. Malm  
30 (U.S. Patents 1,690,620 (1928); 1,690,621 (1928); 1,698,048 (1929); 1,698,049 (1929)) as well as by C.J. Malm and G.D. Hiatt (U.S. Patent 2,172,250 (1939)) suffer from the same shortcomings described above.

E.J. Bourne, M. Stacey, J.C. Tatlow, and J.M.  
35 Tedder (J. Chem. Soc. 1949, 2976-2979) have disclosed

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the use of trifluoroacetic anhydride (TFAA) as an impelling reagent in the acetylation of cellulose and amylose with acetic acid. By their process, a large excess of TFAA (8.4 equivalents/hydroxyl) was required in order to obtain satisfactory yields of the triester. A process for preparing cellulose acetates with a degree of substitution of 0.6-2.8 was not described. Work disclosed by K.S. Barclay, E.J. Bourne, M. Stacey, and M. Webb (J. Chem. Soc. 1954, 1501-1505), T. Morooka, M. Norimoto, T. Yamada, N. Shiraishi (J. Appl. Polym. Sci. 1984, 29, 3981-3990), and T. Yamagishi, T. Fukuda, T. Miyamoto, J. Watanabe (Polym. Bulletin 1988, 20, 373-377) suffer from the same shortcomings described above.

15 In U.S. Patent Application Serial No. 495,186 filed March 19, 1990, C.M. Buchanan teaches the use of trifluoroacetic anhydride and acyl anhydride as an effective means for preparing cellulose triesters as well as less than fully substituted cellulose esters. 20 By this process, smaller amounts of the impelling reagent are required (typically 0.5-1.0 equivalents/hydroxyl) to obtain high molecular weight cellulose ester derivatives with a degree of substitution ranging from 0.5 to 3.0.

25 In U.S. Patent 3,617,201 (1971), R.J. Beral et al. describe a process in which cellulose fiber is treated with TFAA and a carboxylic acid in an inert solvent (benzene) to produce a cellulose ester with a low degree of substitution (0.1-0.3) suitable for use in cellulose 30 textiles. In this process, the cellulose fibers are not disrupted since the reaction medium remains heterogeneous throughout. U.S. Patent 3,097,051 (R.H. Wade, 1963) and S.U. Patent 1,047,908 (O.S. Bludova, N.I. Klenkova, A.P. Sokorenko, 1983) teach similar 35 processes.

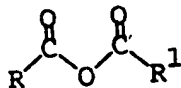
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There is, therefore, a need for a process which provides both cellulose triesters and high hydroxyl cellulose esters having low molecular weight. The process must provide for fast esterification and hydrolysis rates. The process should not require an impelling reagent or excessive amounts of mineral acids. It is desirable that degradation of the cellulose polymer occur in the initial stages of the reaction thereby permitting concentrated reaction mixtures. The process must allow for practical reaction temperatures as well as for easy and practical product and carboxylic acid recovery.

#### Summary of the Invention

Accordingly, we have discovered a process for the preparation of low molecular weight cellulose esters which meets the needs of the cellulose art. Specifically, cellulose triesters (i.e., cellulose esters having a DS of about 3) are rapidly prepared by contacting:

- (a) a cellulose polymer having a degree of substitution less than that of the product cellulose ester (i.e., less than about 3) and also having a molecular weight greater than that of the product cellulose ester,
- (b) trifluoroacetic acid,
- (c) at least one acyl anhydride of the formula:



wherein each of R and R<sup>1</sup> is, independently, H, a straight chain alkyl, branched chain alkyl, aryl, or substituted aryl, and

- (d) a mineral acid,
- in the presence of a solubilizing amount of a solvent and under conditions such that the desired cellulose

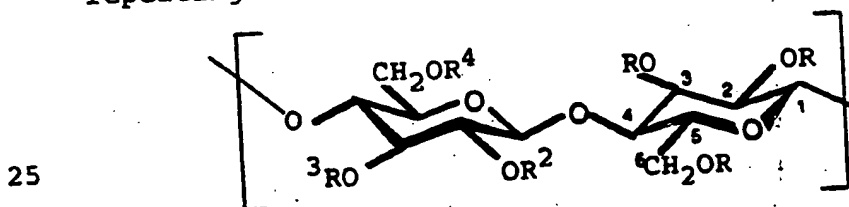
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ester is formed (such process will alternatively be referred to herein as the "triesterification process").

To prepare cellulose esters with a DS of less than about 3, the cellulose triester formed by the above-described process is subjected to a second step (hereinafter alternatively referred to herein as the "hydrolysis step") in which the cellulose triester (i.e., cellulose ester with a DS of about 3) is contacted with a sufficient amount of a reactive hydrolysis solvent under conditions to form the desired cellulose ester with a DS higher than the cellulose polymer used as a starting material for the triesterification process.

#### 15 Detailed Description of the Invention

In accordance with the present invention, typical cellulose esters produced by the process of the invention are C<sub>1</sub> to C<sub>20</sub> esters of cellulose, have the desired DS, have a lower molecular weight than the cellulose polymer starting material, and comprise repeating units of the structure:



wherein R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are selected separately from the group consisting of: hydrogen, straight chain alkanoyl, branched alkanoyl, aroyl, and heteroaroyl.

30 The alkanoyl, aroyl, and heteroaroyl moieties typically contain up to 20 carbon atoms, more typically up to 6 carbon atoms. Preferred cellulose esters produced by the process of the invention include cellulose triacetate, cellulose tripropionate, cellulose



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tributyrate, cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, and cellulose acetate butyrate.

5 The cellulose polymer used as a starting material for preparing the cellulose triester can be cellulose, a secondary cellulose ester, or a mixture thereof. Examples of secondary cellulose esters include cellulose acetate, cellulose propionate, and cellulose butyrate, and are described in U.S. Patent 1 984,147.

10 The cellulose esters useful in the present invention as starting materials have at least 2 anhydroglucose rings and typically have between 2 and 5,000 anhydroglucose rings; also, such polymers typically have an inherent viscosity (I.V.) of about 1.0 to 3.0 deciliters/gram as measured at a temperature of 15 25°C for 0.25 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane. As these I.V. values indicate, such polymers have a molecular weight greater than the product cellulose ester; typical 20 number average molecular weight values range from 1.0 to  $10.0 \times 10^5$ .

The product cellulose esters produced by the process of this invention typically have an inherent viscosity (I.V.) of about 0.2 to about 0.6 25 deciliters/gram as measured at a temperature of 25°C for 0.25 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane and a number average molecular weight of less than about  $1.0 \times 10^5$ .

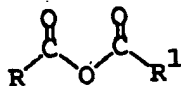
30 The DS of the cellulose polymer starting material for the triesterification process is preferably 0 to about 2.9.

As is known in the art, the theoretical maximum DS for a cellulose ester is 3. However, due to normal error of standard analytical techniques, the maximum DS 35 will vary experimentally, for example an error of plus

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or minus 3 percent is common. When the term "about" is used herein to describe a given DS, it is contemplated that this analytical error will be taken into account as well as minor actual deviations in the DS of the particular cellulose ester. Therefore, it is contemplated that the term "about 3" when referring to a given DS means a measured range of 2.9 to 3.1, preferably 2.95 to 3.05.

Typical anhydrides suitable for the practice of the present invention are of the structure:



wherein each of R and R<sup>1</sup> is, independently, selected from the group consisting of hydrogen, a straight chain alkyl, a branched chain alkyl, aryl or substituted aryl. In the acyl anhydride molecule, typical straight chain alkyl groups contain 1 to 20 carbon atoms, typical branched chain alkyl groups have 3 to 20 carbon atoms, and typical aryl groups have 6 to 12 carbon atoms. Substituted aryl groups are typically substituted with 1, 2 or 3 substituents such as lower alkyl (i.e., alkyl groups having 1 to 3 carbon atoms), halo (i.e., F, Br, Cl or I), and lower alkoxy (i.e., alkoxy groups having 1 to 3 carbon atoms). It is preferred that the acyl anhydride is symmetrical, i.e., that R and R<sup>1</sup> are the same.

Exemplary acyl anhydrides useful in the present invention are, but are not limited to, acetic anhydride, propionic anhydride, isobutyric anhydride, butyric anhydride, trimethylacetic anhydride, valeric anhydride, hexanoic anhydride, nonanoic anhydride, benzoic anhydride, or a mixture thereof. The most preferred acyl anhydrides include acetic anhydride, propionic anhydride, butyric anhydride, or a mixture thereof.

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The mineral acid useful as component (d) in the present invention can be any strong mineral acid which, when combined with trifluoroacetic acid (TFA), promotes rapid esterification, hydrolysis, and molecular weight loss. Examples of such mineral acids include sulfuric acid, hydrochloric acid,  $\text{Mg}(\text{ClO}_4)_2$  and  $\text{HClO}_4$ . Of course, mixtures of two or more mineral acids are contemplated for use in the present invention.

In the process of preparing the cellulose triester the amount of component (b) (i.e., the TFA) is preferably about 0.25 to 1.0 equivalents per hydroxyl, more preferably about 1.0 equivalents; the amount of component (c) is preferably at least 1.0 equivalent per hydroxyl, more preferably about 1.7 equivalents; and the amount of component (d) is preferably about 0.0001 to 0.01 equivalents per hydroxyl, more preferably about 0.008 equivalents.

Conditions suitable for the formation of cellulose esters can vary widely. The temperature typically varies from ambient to the temperature at which the mixture begins to reflux; typically about 20°C to about 150°C. More preferably, the temperature is 70°C.

Those skilled in the art readily recognize that contact time and acyl anhydride reactivity are interdependent. For example, acylation with a mixture of propionic anhydride and acetic anhydride requires a contact time as little as 5 minutes. When acylating the same wood pulp with a mixture of butyric acid and acetic anhydride, a contact time of 30 minutes may be required.

Those skilled in the art understand that the flat period (i.e., the period of time after formation of the cellulose triester and beginning of hydrolysis during which polymer degradation is occurring) can vary widely. Accordingly, a broad flat period for the

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process of the invention is about 1 minute to about 120 minutes. A more preferred flat period is about 5 minutes to about 30 minutes.

Thus, the total reaction period of time (i.e., including the period for acylation, flat period, and hydrolysis period), can vary from about 0.5 to about 25 hours. A preferred total reaction period is about 4 to about 8 hours.

The mixture of the TFA and the mineral acid in the triesterification process essentially acts as a catalyst. In addition, the mineral acid functions to degrade the cellulose polymer. By utilizing a mineral acid in the triesterification process, molecular weight loss occurs during formation of the cellulose triester which permits more concentrated reaction mixtures and thereby easier isolation of the product cellulose ester.

For the triesterification process said solvent is typically a carboxylic acid having 1 to 20 carbon atoms, dimethylformamide, dimethylsulfoxide, or a mixture thereof; however, excess acyl anhydride can be used as solvent. The carboxylic acid can optionally be substituted with halogen atoms such as F, Br, and Cl; an example of such a substituted carboxylic acid is trifluoroacetic acid. Preferred is a carboxylic acid, especially the particular carboxylic acid corresponding to the acyl anhydride(s) employed, or, in the case of mixed esters, corresponding to the least reactive acyl anhydride.

If a carboxylic acid is used as a reaction solvent, the acid can contribute to the reaction (i.e., act as a reactant) if the particular carboxylic acid used has a corresponding anhydride that is more reactive than the acyl anhydride employed as reactant (c).

The reactive hydrolysis solvent for the hydrolysis step is typically a polar solvent such as an n-alkanol

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having 1 to 4 carbon atoms, water, a branched chain alkanol having 3 to 4 carbon atoms, an aryl alkanol having 7 to 12 carbon atoms, and a mixture thereof.

Preferred reactive hydrolysis solvents include  
5 methanol, ethanol, n-propanol, n-butanol, isopropyl alcohol, benzyl alcohol, water, or a mixture thereof. Most preferred are methanol and water, or a mixture thereof.

For the hydrolysis step, the preferred amount of  
10 reactive hydrolysis solvent is from about 1 volume % to that amount which results in the desired product precipitating from solution. It is more preferred that the amount of reactive hydrolysis solvent is from about 5 to about 15 volume %.

Preferred reaction conditions for the hydrolysis  
15 step include a temperature range from ambient to the temperature at which the mixture begins to reflux (typically 20°C to 150°C) and a reaction time of about 0.5 hours to about 24 hours. Most preferred reaction  
20 conditions are a temperature of 70°C and a reaction time of about 4 hours to about 7 hours.

The cellulose triester formed by the triesterification process can be isolated and/or purified by  
25 conventional means known in the art such as by precipitation into a nonsolvent, distillation, or by spray drying (and, if desired, subjected to the hydrolysis step). Alternatively, the cellulose triester can be hydrolyzed directly in the reaction medium without the need for any special purification or  
30 isolation steps. After hydrolysis, the desired cellulose ester can be isolated and purified by conventional means known in the art, such as by a nonsolvent precipitation, distillation, or by spray drying.

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The preferred cellulose esters produced after the hydrolysis step are substantially the same as produced by the triesterification process except that the DS is lower. Thus, preferred products produced by the hydrolysis step include cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate propionate, and cellulose acetate butyrate.

Typical desired products produced after the hydrolysis step of the invention have a DS of about 0.5 to about 2.85, more typically about 1.9 to about 2.3 (for mixed esters, the DS refers to the combined DS).

The cellulose esters produced by the triesterification process (optionally followed by the hydrolysis step) have low molecular weight. Typical molecular weight ranges of cellulose esters produced by the process of the present invention have a number average molecular weight ( $M_n$ ) of about  $0.01 \times 10^5$  to about  $1.0 \times 10^5$ , a weight average molecular weight ( $M_w$ ) of about  $0.02 \times 10^5$  to about  $2.0 \times 10^5$ , and a Z average molecular weight ( $M_z$ ) of about  $0.04 \times 10^5$  to about  $4.0 \times 10^5$ . Preferred molecular weight ranges are an  $M_n$  of about  $0.2 \times 10^5$  to about  $0.6 \times 10^5$ , a  $M_w$  of about  $0.6 \times 10^5$  to about  $1.0 \times 10^5$ , and a  $M_z$  of about  $0.3 \times 10^5$  to about  $3.0 \times 10^5$ . The ratio of  $M_w/M_n$  is preferably about 1.0 to about 2.0, with about 1.4 to about 1.9 being more preferred.

As is well known in the art, I.V. values are related to molecular weight. The I.V. of the product cellulose ester produced by the triesterification process (optionally followed by the hydrolysis step) is typically about 0.2 to about 0.6, preferably about 0.3 to about 0.4 deciliters/gram as measured at a temperature of 25°C for 0.25 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane.

Some products produced after the hydrolysis step,

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especially high hydroxyl (i.e., low DS), mixed esters, will be soluble in n-propylacetate (n-PrOAc), acetone,  $\text{CHCl}_3$ , ethanol, tetrahydrofuran (THF), and dimethylsulfoxide (DMSO).

- 5       The following examples are to illustrate the invention but should not be interpreted as a limitation thereon.

#### EXAMPLES

- 10       In the following examples, water activated cellulose was prepared by mechanically blending the cellulose with water. The excess water was removed by filtration. Residual water was removed by washing the damp cellulose with the carboxylic acid which
- 15       corresponds to an acyl group being attached to the cellulose polymer. The activated cellulose was loaded into a flask equipped for mechanical stirring. To the cellulose was added a mixture of acyl anhydride(s) and a catalyst consisting of TFA and a mineral acid such as
- 20       sulfuric acid. The reactor was then heated to 70°C. The reaction mixture was stirred until a clear solution was obtained which is the indicated contact time for formation of the triester. After formation of the triester, the reaction mixture was maintained at 70°C
- 25       for a period of time to allow degradation of the polymer (i.e., a flat period) before adding a hydrolysis solution to the reaction mixture. The reaction was stirred for the indicated time(s) before isolating the product by addition of a nonsolvent. The TFA, the
- 30       carboxylic acid(s), and the unconsumed acyl anhydride(s) can be recovered from the reaction mixture before the addition of a nonsolvent. Also, the TFA and carboxylic acids can be recovered from the filtrate following precipitation by distillation techniques familiar to
- 35       those skilled in the art. Alternatively, the TFA, the

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carboxylic acid(s), and the unconsumed acyl anhydride(s) can be isolated by spray drying techniques familiar to those skilled in the art. The results in the examples indicate yields of isolated, well-

5 characterized products. The products were typically characterized by proton NMR spectroscopy, inherent viscosity, gel permeation chromatography (values are reported in polystyrene equivalents), and other methods familiar to those skilled in the art. The abbreviations

10 used herein have the following meanings: TFA is trifluoroacetic acid, TFAA is trifluoroacetic anhydride, NMR is nuclear magnetic resonance, Pr DS is propionyl degree of substitution, Ac DS is acetyl degree of substitution, TCE is tetrachloroethane, GPC is gel

15 permeation chromatography, DMF is dimethylformamide, THF is tetrahydrofuran, DMSO is dimethylsulfoxide, n-ProAc is propyl acetate, and CAB is cellulose acetate butyrate.

20 EXAMPLE 1

Reagents set forth below were subjected to the standard procedure described above under the indicated reaction conditions. The result, in terms of identity and yield of the desired cellulose ester, and key

25 analyses of the product, are also set forth below.



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	Starting Cellulosic Weight (g)	Cellulose	50	
5	Equivalents of TFA/hydroxyl		1.0	
	Equivalents of H <sub>2</sub> SO <sub>4</sub> /hydroxyl		0.008	
10	Acyl Anhydride Equivalents/hydroxyl	Acetic Anhydride	0.03	
	Acyl Anhydride Equivalents/hydroxyl	Propionic Anhydride	1.7	
15	Carboxylic Acid Weight (g)	Propionic Acid	107	
	Hydrolysis Mixture	76.5 g water		
20	Contact Time (min)		10	
	Flat Period (min)		30	
25	Hydrolysis Time (h)	Pr DS ( <sup>1</sup> H NMR)	Ac DS ( <sup>1</sup> H NMR)	I.V. (Phenol/TCE)
	0	3.00	0.05	0.35
	2.0	2.59	0.03	0.37
	4.0	2.24	0.02	0.39
	5.0	2.06	0.01	0.41
30	6.0	1.93	0.01	0.42
	7.0	1.84	0.01	0.42
	7.8	1.70	0.01	0.44

35 This example demonstrates that a catalyst system consisting of TFA/H<sub>2</sub>SO<sub>4</sub> rapidly promotes the esterification of cellulose with propionic anhydride and acetic anhydride to provide a triester, provides for rapid degradation of the cellulose polymer, and gives

40 excellent rates of hydrolysis.

- 15 -

EXAMPLE 2.

Reagents set forth below were subjected to the standard procedure described above under the indicated reaction conditions. The result, in terms of identity and yield of the desired cellulose ester, and key analyses of the product, are also set forth below.

10	Starting Cellulosic Weight (g)	Cellulose	50	
	Equivalents of TFA/hydroxyl		1.0	
15	Equivalents of $\text{Mg}(\text{ClO}_4)_2$ /hydroxyl		0.008	
	Acyl Anhydride Equivalents/hydroxyl	Acetic Anhydride	0.03	
20	Acyl Anhydride Equivalents/hydroxyl	Propionic Anhydride	1.7	
	Carboxylic Acid Weight (g)	Propionic Acid	86	
25	Hydrolysis Mixture	76.5 g water		
	Contact Time (min)	7		
30	Flat Period (min)	9		
35	Hydrolysis Time (h)	Pr DS ( $^1\text{H}$ NMR)	Ac DS ( $^1\text{H}$ NMR)	I.V. (Phenol/TCE)
	0	3.05	0.04	0.54
	1.0	2.77	0.04	0.34
	1.8	2.51	0.02	0.34
	3.3	2.16	0.00	0.36
	5.3	1.79	0.01	0.38
	6.3	1.59	0.00	0.39

40

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This example demonstrates that a catalyst system consisting of TFA/Mg(ClO<sub>4</sub>)<sub>2</sub> rapidly promotes the esterification of cellulose with propionic anhydride and acetic anhydride to provide a triester, provides for rapid degradation of the cellulose polymer, and gives excellent rates of hydrolysis.

**EXAMPLE 3**

10 Reagents set forth below were subjected to the standard procedure described above under the indicated reaction conditions. The result, in terms of identity and yield of the desired cellulose ester, and key analyses of the product, are also set forth below.

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	Starting Cellulosic Weight (g)	Cellulose 50
5	Equivalents of TFA/hydroxyl	1.0
	Equivalents of H <sub>2</sub> SO <sub>4</sub> /hydroxyl	0.008
10	Acyl Anhydride Equivalents/hydroxyl	Acetic Anhydride 0.03
	Acyl Anhydride Equivalents/hydroxyl	Propionic Anhydride 1.7
15	Carboxylic Acid Weight (g)	Propionic Acid 75
	Hydrolysis Mixture	76.5 g water
20	Contact Time (min)	5
	Flat Period (min)	30
25	Hydrolysis Time (h)	4.5
	DS Pr( <sup>1</sup> H NMR)	2.08
	DS Ac( <sup>1</sup> H NMR)	0.02
30	GPC (DMF/LiBr, Polystyrene equivalents)	$M_n = 0.4 \times 10^5$ ; $M_w = 0.7 \times 10^5$ ; $M_z = 0.4 \times 10^5$ ; $M_w/M_n = 1.92$
35	IV (Phenol/TCE)	0.33
	Solubility Data	Soluble in organic solvents such as n-PrOAc, acetone, CHCl <sub>3</sub> , THF, alcohol, and DMSO
40		

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This example demonstrates that a catalyst system consisting of TFA/H<sub>2</sub>SO<sub>4</sub> can be used to obtain a CAP mixed ester with high hydroxyl content and low molecular weight. This mixed ester gives high solids to liquid ratios in organic solvents such as n-propyl acetate (25%).

**EXAMPLE 4**

Reagents set forth below were subjected to the standard procedure described above under the indicated reaction conditions. The result, in terms of identity and yield of the desired cellulose ester, and key analyses of the product, are also set forth below.

15	Starting Cellulosic Weight (g)	Cellulose 50
	Equivalents of TFA/hydroxyl	1.0
20	Equivalents of H <sub>2</sub> SO <sub>4</sub> /hydroxyl	0.008
	Acyl Anhydride Equivalents/hydroxyl	Acetic Anhydride 0.03
25	Acyl Anhydride Equivalents/hydroxyl	Butyric Anhydride 1.7
30	Carboxylic Acid Weight (g)	Butyric Acid 75
	Hydrolysis Mixture	76.5 g water
35	Contact Time (min)	15
	Flat Period (min)	30

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Hydrolysis	Bu DS	Ac DS	I.V.
<u>Time (h)</u>	<u>(<sup>1</sup>H NMR)</u>	<u>(<sup>1</sup>H NMR)</u>	<u>(Phenol/TCE)</u>
0	3.02	0.07	0.40
2.0	2.74	0.06	0.37
5 4.0	2.43	0.04	0.36
5.0	2.36	0.03	0.37
6.0	2.28	0.03	0.35
7.0	2.12	0.02	0.40

- 10 This example demonstrates that a catalyst system consisting of TFA/H<sub>2</sub>SO<sub>4</sub> rapidly promotes the esterification of cellulose with butyric anhydride and acetic anhydride to provide a triester, provides for rapid degradation of the cellulose polymer, and gives
- 15 excellent rates of hydrolysis.

#### EXAMPLE 5

- 20 Reagents set forth below were subjected to the standard procedure described above under the indicated reaction conditions. The result, in terms of identity and yield of the desired cellulose ester, and key analyses of the product, are also set forth below.

- 20 -

	Starting Cellulosic Weight (g)	Cellulose 50
5	Equivalents of TFA/hydroxyl	1.0
	Equivalents of H <sub>2</sub> SO <sub>4</sub> /hydroxyl	0.008
10	Acyl Anhydride Equivalents/hydroxyl	Acetic Anhydride 0.07
	Acyl Anhydride Equivalents/hydroxyl	Butyric Anhydride 1.7
15	Carboxylic Acid Weight (g)	Butyric Acid 75
	Hydrolysis Mixture	76.5 g water
20	Contact Time (min)	25
	Flat Period (min)	30
25	Hydrolysis Time (h)	7
	DS Bu( <sup>1</sup> H NMR)	2.18
	DS Ac( <sup>1</sup> H NMR)	0.06
30	GPC (DMF/LiBr, Polystyrene equivalents)	$M_n = 0.5 \times 10^5$ ; $M_w = 1.0 \times 10^5$ ; $M_z = 1.5 \times 10^5$ ; $M_w/M_n = 1.45$
35	IV (Phenol/TCE)	0.39
	Solubility Data	Soluble in organic solvents such as n-ProAc, acetone, CHCl <sub>3</sub> , THF, alcohol, and DMSO
40		

- 21 -

This example demonstrates that a catalyst system consisting of TFA/H<sub>2</sub>SO<sub>4</sub> can be used to obtain a CAB mixed ester with high hydroxyl content and low molecular weight. This mixed ester gives high solids to liquid ratios in organic solvents such as n-propyl acetate (25%).

**EXAMPLE 6**

Reagents set forth below were subjected to the standard procedure described above under the indicated reaction conditions. The result, in terms of identity and yield of the desired cellulose ester, and key analyses of the product, are also set forth below.

15	Starting Cellulosic Weight (g)	Cellulose 50
	Equivalents of TFAA/hydroxyl	1.5
20	Acyl Anhydride Equivalents/hydroxyl	Acetic Anhydride 0.15
25	Acyl Anhydride Equivalents/hydroxyl	Propionic Anhydride 1.7
	Carboxylic Acid Weight (g)	Propionic Acid 152
30	Hydrolysis Mixture	76.5 g water, 152 g Propionic Acid
	Contact Time (min)	1080
35	Reaction Temperature	55°C



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Hydrolysis Time (h)	Pr DS	Ac DS	I.V.
	( <sup>1</sup> H NMR)	( <sup>1</sup> H NMR)	(Phenol/TCE)
0	3.04	0.09	1.44
2.2	2.90	0.08	1.37
4.7	2.63	0.10	1.37
7.2	2.46	0.08	1.38

10 This example differs from the standard procedure in that the sulfuric acid was omitted, TFAA was substituted for TFA, and the reaction was at 55°C. The result is a longer contact time, slower hydrolysis rate, and higher molecular weights as illustrated by I.V.

15 With reference to Example 1, this example demonstrates the critical role of sulfuric acid and illustrates how the process of this invention differs from a process devoid of sulfuric acid and TFA.

EXAMPLE 7 (Comparative)

20 Reagents set forth below were subjected to the standard procedure described above under the indicated reaction conditions. The result, in terms of identity and yield of the desired cellulose ester, and key analyses of the product, are also set forth below.

- 23 -

	Starting Cellulosic Weight (g)	Cellulose 5
5	Equivalents of TFA/hydroxyl	0.8
	Acyl Anhydride Equivalents/hydroxyl	Acetic Anhydride 2.1
10	Carboxylic Acid Weight (g)	Acetic Acid 30
	Contact Time (min)	10320
15	Reaction Temperature	55°C
	Product	Cellulose Triacetate
20	Degree of Substitution (From $^1\text{H}$ NMR)	3.02
	Intrinsic Viscosity (Phenol/TCE)	1.74
25	GPC (DMF, Polystyrene equivalents)	$M_n = 25.7 \times 10^4$ ; $M_w = 4.4 \times 10^5$ $M_z = 7.6 \times 10^5$ ; $M_w/M_n = 170$

30 This example differs from the standard procedure in that the sulfuric acid was omitted and the reaction was at 55°C.

With reference to Examples 1 and 6, this example demonstrates the critical role of sulfuric acid and illustrates how the process of this invention differs from a process using TFA but devoid of sulfuric acid.

#### 35 EXAMPLE 8 (Comparative)

Reagents set forth below were subjected to the standard procedure described above under the indicated reaction conditions. The result, in terms of identity and yield of the desired cellulose ester, and key analyses of the product, are also set forth below.

40

- 24 -

- |    |   |                       |
|----|---|-----------------------|
|    | Starting Cellulosic Weight (g)                          | Cellulose<br>50       |
| 5  | Equivalents of TFA/hydroxyl                             | 1.0                   |
|    | Equivalents of H <sub>2</sub> SO <sub>4</sub> /hydroxyl | 0.008                 |
| 10 | Carboxylic Acid Weight (g)                              | Acetic Acid<br>1.9    |
|    | Carboxylic Acid Weight (g)                              | Propionic Acid<br>230 |
| 15 | Contact Time (min)                                      | 1510                  |
|    | DS (From <sup>1</sup> H NMR)                            | No Reaction           |
- 20 This example differs from the standard procedure in that the appropriate molar amount of carboxylic acid was substituted for the acyl anhydrides.
- With reference to Example 1, this example demonstrates the critical role of acyl anhydrides and
- 25 illustrates an aspect of how this process differs from that taught by H.T. Clarke and C.J. Malm (U.S. Patent 1,880,808 (1932)).
- The invention has been described in detail with particular reference to preferred embodiments thereof,
- 30 but it will be understood that variations and modifications can be effected within the spirit and scope of the invention. All of the U.S. patents cited in the specification are incorporated herein by reference in their entirety.

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- 25 -

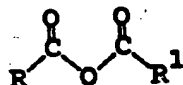
Claims

We Claim:

- 5 1. A process for preparing cellulose esters having a degree of substitution of 3 and a number average molecular weight of less than  $1.0 \times 10^5$  comprising contacting the following:

- 10 (a) a cellulose polymer having a degree of substitution less than that of the product cellulose ester and molecular weight greater than that of the product cellulose ester,  
(b) trifluoroacetic acid,  
(c) at least one acyl anhydride of the formula:

15



wherein each of R and R<sup>1</sup> is, independently, H, a straight chain alkyl, a branched chain alkyl, aryl, or substituted aryl, and

- 20 (d) a mineral acid,  
in the presence of a solubilizing amount of a solvent and under conditions such that the desired cellulose ester is formed.

- 25 2. The process of Claim 1 wherein component (a) is a cellulose polymer having a degree of substitution of 0 to 2.9 and is selected from the group consisting of cellulose, a secondary cellulose ester, and a mixture thereof.

30

3. The process of Claim 1 wherein component (c) is selected from the group consisting of acetic anhydride, propionic anhydride, isobutyric anhydride, butyric anhydride, trimethylacetic

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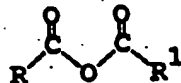
anhydride, valeric anhydride, hexanoic anhydride, nonanoic anhydride, benzoic anhydride, and a mixture thereof.

- 5      4. The process of Claim 1 wherein the amount of component (b) is 0.25 to 1.0 equivalents per hydroxyl, the amount of component (c) is at least 1 equivalent per hydroxyl, and the amount of component (d) is 0.0001 to 0.01 equivalents per hydroxyl.
- 10
- 15      5. The process of Claim 1 wherein component (c) is selected from the group consisting of acetic anhydride, propionic anhydride, butyric anhydride, and a mixture thereof.
- 20      6. The process of Claim 1 carried out at 20°C to 150°C for 5 to 30 minutes.
- 25      7. The process of Claim 1 wherein said solvent is selected from the group consisting of a carboxylic acid having 1 to 20 carbon atoms, dimethylformamide, dimethylsulfoxide, and a mixture thereof.
- 30      8. The process of Claim 1 wherein said solvent is acetic acid.
- 35      9. The process of Claim 1 wherein R and R<sup>1</sup> are the same.
10. The process of Claim 1 including the additional step of isolating, after reaction, the desired product by the addition of a precipitating amount of a nonsolvent, distillation, or by spray drying.

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11. The process of Claim 1 wherein component (d) is selected from the group consisting of hydrochloric acid,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{HClO}_4$ , and a mixture thereof.
- 5 12. The process of Claim 1 wherein the product cellulose ester has a  $M_n$  of  $0.01 \times 10^5$  to  $1.0 \times 10^5$ , a  $M_w$  of  $0.02 \times 10^5$  to  $2.0 \times 10^5$ , a  $M_z$  of  $0.04 \times 10^5$  to  $4.0 \times 10^5$ , and a ratio of  $M_w/M_n$  of 1.0 to 2.0.
- 10 13. The process of Claim 1 wherein the product cellulose ester has a  $M_n$  of  $0.2 \times 10^5$  to  $0.6 \times 10^5$ , a  $M_w$  of  $0.6 \times 10^5$  to  $1.0 \times 10^5$ , a  $M_z$  of  $0.3 \times 10^5$  to  $3.0 \times 10^5$ , and a ratio of  $M_w/M_n$  of 1.5 to 1.9.
- 15 14. The process of Claim 1 wherein the product cellulose ester is cellulose triacetate, cellulose tributyrate, cellulose tripropionate, cellulose acetate butyrate, cellulose acetate propionate, and said product cellulose ester has an inherent viscosity of 0.2 to 0.6 as measured at a temperature of  $25^\circ\text{C}$  for a 0.25 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane.
- 20 15. A process for preparing a cellulose ester having a degree of substitution of less than 3 and a number average molecular weight of less than  $1.0 \times 10^5$  comprising:
- 25 (A) contacting
- 30 (a) a cellulose polymer having a degree of substitution of less than 3,
- (b) trifluoroacetic anhydride,
- (c) at least one acyl anhydride of the formula:
- 35

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wherein each of R and R<sup>1</sup> is,  
independently, H, a straight chain alkyl,  
a branched alkyl, aryl, or substituted  
aryl, and

(d) a mineral acid,

in the presence of a solubilizing amount of a  
solvent and under condition such that a  
cellulose ester is formed having a degree of  
substitution of 3 and a molecular weight less  
than that of the cellulose polymer of  
step (A)(a), and

(B) contacting the cellulose ester formed by  
step (A) with a sufficient amount of a  
reactive hydrolysis solvent under conditions  
to form the desired cellulose ester which has  
a degree of substitution higher than the  
original cellulose polymer of step (A)(a).

16. The process of Claim 15 wherein for step (A),  
component (a) is a cellulose polymer having a  
degree of substitution of 0 to 2.9 and is selected  
from the group consisting of cellulose, a secondary  
cellulose ester, and a mixture thereof.

17. The process of Claim 15 wherein for step (A),  
component (c) is selected from the group consisting  
of acetic anhydride, propionic anhydride,  
isobutyric anhydride, butyric anhydride,  
trimethylacetic anhydride, valeric anhydride,  
hexanoic anhydride, nonanoic anhydride, benzoic  
anhydride, and a mixture thereof.

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18. The process of Claim 15 wherein for step (A), the amount of component (b) is 0.25 to 1.0 equivalents per hydroxyl, the amount of component (c) is at least 1 equivalent per hydroxyl, and the amount of component (d) is 0.0001 to 0.01 equivalents per hydroxyl.
19. The process of Claim 15 wherein for step (A), component (c) is selected from the group consisting of acetic anhydride, propionic anhydride, butyric anhydride, and a mixture thereof.
20. The process of Claim 15 wherein step (A) is carried out at 20°C to 150°C for 5 to 30 minutes.
21. The process of Claim 15 wherein said reactive hydrolysis solvent is selected from the group consisting of an n-alkanol having 1 to 4 carbon atoms, water, a branched chain alkanol having 3 to 4 carbon atoms, an aryl alkanol having 7 to 12 carbon atoms, and a mixture thereof.
22. The process of Claim 15 wherein said reactive hydrolysis solvent is selected from the group consisting of methanol, ethanol, n-propanol, n-butanol, isopropyl alcohol, benzyl alcohol, and water.
23. The process of Claim 15 wherein said reactive hydrolysis solvent is selected from the group consisting of methanol, water, and a mixture thereof.
24. The process of Claim 15 wherein the amount of reactive hydrolysis solvent is from 1 volume % to



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that amount which results in the desired product precipitating from solution.

- 5 25. The process of Claim 15 wherein the amount of reactive hydrolysis solvent is from 5 to 15 volume %.
- 10 26. The process of Claim 15 wherein step (B) is carried out at a temperature from 20°C to 150°C for 0.5 to 24 hours.
- 15 27. The process of Claim 15 wherein the cellulose ester formed by step (B) has a degree of substitution of from 0.5 to 2.85.
- 20 28. The process of Claim 15 wherein the solvent for step (A) is selected from the group consisting of a carboxylic acid having 1 to 20 carbon atoms, dimethylformamide, dimethylsulfoxide, and a mixture thereof.
- 25 29. The process of Claim 15 wherein the solvent for step (A) is acetic acid.
- 30 30. The process of Claim 15 wherein R and R<sup>1</sup> are the same.
31. The process of Claim 15 including the additional step of isolating, after reaction, the desired product by the addition of a precipitating amount of a nonsolvent, distillation, or spray drying.

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32. The process of Claim 15 wherein the mineral acid for step (A) is selected from the group consisting of hydrochloric acid,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{HClO}_4$ , and a mixture thereof.

5

33. The process of Claim 15 wherein the cellulose ester produced by step (A) has a  $M_n$  of  $0.01 \times 10^5$  to  $1.0 \times 10^5$ , a  $M_w$  of  $0.02 \times 10^5$  to  $2.0 \times 10^5$ , a  $M_z$  of  $0.04 \times 10^5$  to  $4.0 \times 10^5$ , and a ratio of  $M_w/M_n$  of 1.0 to 2.0.

10

34. The process of Claim 15 wherein the cellulose ester produced by step (A) has a  $M_n$  of  $0.2 \times 10^5$  to  $0.6 \times 10^5$ , a  $M_w$  of  $0.6 \times 10^5$  to  $2.0 \times 10^5$ , a  $M_z$  of  $0.3 \times 10^5$  to  $3.0 \times 10^5$ , and a ratio of  $M_w/M_n$  of 1.5 to 1.9.

15

35. The process of Claim 15 wherein the final product cellulose ester is cellulose acetate, cellulose butyrate, cellulose propionate, cellulose acetate butyrate, cellulose acetate propionate, and said product cellulose ester has an inherent viscosity of 0.2 to 0.6 as measured at a temperature of  $25^\circ\text{C}$  for a 0.25 gram sample in 100 ml of a 60/40 by weight solution of phenol/tetrachloroethane.

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36. The process of Claim 15 wherein the total reaction period is 0.5 to 25 hours.

30

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/02557

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>5</sup> : C 08 B 3/02, C 08 B 3/06, C 08 B 3/24																	
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; text-align: left; border-bottom: 1px solid black;">Classification System</th> <th style="text-align: left; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">IPC<sup>5</sup></td> <td style="border: 1px solid black; padding: 5px;">C 08 B</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	IPC <sup>5</sup>	C 08 B											
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IPC <sup>5</sup>	C 08 B																
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; text-align: left; border-bottom: 1px solid black;">Category <sup>10</sup></th> <th style="text-align: left; border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 15%; text-align: left; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 2629716 (P.W. MORGAN) 24 February 1953 see the whole document ---</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-36</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">US, A, 1645915 (C.J. MALM) 18 October 1927 see page 1, lines 57-62; claims ---</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-36</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;">WPIL, week 8914, AN 89-105406/14, 17 May 1989; Derwent Publications, (GB), &amp; SU, A, 1426974 (PHYS. CHEM. PROBLEMS), 19 September 1986 see the whole document ---</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-36</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">P, A</td> <td style="padding: 5px;">Chemical Patents Index, week 9037, 7 November 1990, AN 90-280997/37, Derwent Publications, (GB), &amp; SU, A, 1525168 (ALTAI UNIV.), 30 November 1989 see yhe whole abstract ./.</td> <td></td> </tr> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	Y	US, A, 2629716 (P.W. MORGAN) 24 February 1953 see the whole document ---	1-36	Y	US, A, 1645915 (C.J. MALM) 18 October 1927 see page 1, lines 57-62; claims ---	1-36	Y	WPIL, week 8914, AN 89-105406/14, 17 May 1989; Derwent Publications, (GB), & SU, A, 1426974 (PHYS. CHEM. PROBLEMS), 19 September 1986 see the whole document ---	1-36	P, A	Chemical Patents Index, week 9037, 7 November 1990, AN 90-280997/37, Derwent Publications, (GB), & SU, A, 1525168 (ALTAI UNIV.), 30 November 1989 see yhe whole abstract ./.	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>14</sup> Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents; such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </div> </div>																	
<b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of the Actual Completion of the International Search  <div style="text-align: center;">27th June 1991</div> </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;">           Date of Mailing of this International Search Report  <div style="text-align: center;">09.08.91</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;">           International Searching Authority  <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; padding: 5px;">           Signature of Authorized Officer  <div style="text-align: center;">F.W. HECK </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">27th June 1991</div>	Date of Mailing of this International Search Report <div style="text-align: center;">09.08.91</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;">F.W. HECK </div>											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>GB, A, 2105725 (DAICEL CHEMICAL) 30 March 1983</p> <p>-----</p>	

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9102557  
SA 47750

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 12/07/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 2629716		None	
US-A- 1645915		None	
GB-A- 2105725	30-03-83	JP-C- 1293640	16-12-85
		JP-A- 53011501	22-01-83
		JP-B- 60017441	02-05-85
		US-A- 4415734	15-11-83